



On the Morphological Changes of Ni- and Ni(Pt)-Silicides

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The issue of agglomeration and layer inversion has remained critical because conductivity of thin silicide films is sensitive to the degradation of the film morphology. The purpose of this work is to study the morphology degradation that includes agglomeration and layer inversion of NiSi and Ni(Pt)Si. Agglomeration was observed to be preceded by holes evolution. It was found that the addition of Pt has led to improvement in the agglomeration behavior of NiSi but have little influence on the layer inversion when the amount of Pt is 5 atom % in Ni(Pt) on the undoped poly-Si. Increasing the Pt concentration to about 10% shows improvement in the layer inversion behavior compared to 5% Pt. The agglomeration behavior and layer inversion with the addition of the Pt are discussed in terms of the controlling factors of grain boundary energy, interface energies, and nature of the silicide formed. The improved agglomeration associated with Pt addition is attributed to a lower interfacial energy leading to lower grain boundary mobility and reduced driving force for hole evolutions. In addition, suppression of layer inversion can be attained by silicidation with the use of thin Ni(Pt) (~10 nm).

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NiSi is one candidate for the replacement of CoSi₂ as contacts to the source, drain, and gates of complementary metal oxide semiconductor (CMOS) devices due to a single-step low-temperature formation, low resistivity and low Si consumption. However, challenges remain to the integration of NiSi process and requires certain extent of attention. This includes avoiding the formation of NiSi₂, a high resistivity phase, which forms at ~750°C and how to increase the morphology stability of NiSi. To enhance the phase stability of NiSi, Pt is added and it has been shown to form monosilicide, *i.e.*, Ni(Pt)Si even up to 900°C.¹ The application of Ni(Pt)Si to devices at silicidation temperatures above 700°C has also been demonstrated.² On the other hand, the issue of agglomeration and layer inversion has remained a critical issue because conductivity of thin silicide films is sensitive to the degradation of the film morphology. In addition to the agglomeration of silicides, the stability of Ni silicides on poly-Si can be disrupted by the phenomenon of layer inversion, during which the layer reversal of the silicide and poly-Si bilayer occurs at temperature as low as 550°C.³

During the layer reversal, an abrupt increment in tensile stress in NiSi/poly-Si at 550°C was observed and grain growth from 25 to 300 nm was reported.⁴ This is due to the additional driving force for morphological changes arising from the grain boundary energy of the poly-Si. The process starts with the growth of the poly-Si grains of many orientations into silicide, and the energetically favored poly-Si grains [*e.g.*, (111) orientation] will grow faster through the top silicide layer.⁵ The surface energy and interface energy of the poly-Si are also important in view of the changes in texture after grain growth of poly-Si from (110) to (111) which gives a lower surface energy than other orientations. The presence of silicide provides a fast diffusion path for the transport of material and therefore enhances the grain growth of poly-Si. This causes severe roughening of the silicide/poly-Si interface and eventually leads to the inversion of the two layers.

This work aims to study the morphology degradation of pure NiSi and Ni(Pt)Si. It is of technological interest to characterize and investigate the effect of Pt addition on the agglomeration behavior and layer inversion tendency. Rutherford backscattering spectroscopy (RBS), scanning electron microscopy (SEM), cross-sectional transmission electron microscopy (XTEM), and electron diffraction analysis were employed to study the morphological degradation that includes agglomeration and layer inversion of NiSi and Ni(Pt)Si.

Experimental

Silicidation was done on Si(100) and undoped poly-Si substrates. The undoped poly-Si was deposited by low-pressure chemical vapor deposition (LPCVD) on ~6 nm thick oxide grown by furnace oxidation of the p-type (100) Si. The as-deposited poly-Si consists of small, needlelike grains. Following a dilute HF dip, Ni and Ni(Pt) films of various thickness were sputter deposited. The Pt concentration in Ni(Pt) is 5 atom %. In addition, a 10 atom % Ni(Pt) alloy is also sputtered onto poly-Si substrates. Rapid thermal annealing (RTA) was carried out in a N₂ ambient at temperatures ranging from 500 to 900°C for 30–60 s. The morphological changes were studied using SEM, RBS, and XTEM. The SEM analysis in this work was performed using an accelerating voltage of 10 keV with a working distance of ~5 mm was used. In the experiment of RBS, the back-scattered particles were detected at a scattering angle of 160° using a 50 mm² PIP detector at an energy resolution of 14 keV. The XTEM was performed at an accelerating voltage of 200 keV with a spot size about 2 nm.

Results

Agglomeration.—Figures 1a and b show the SEMs of silicide formed at 600 and 700°C using as-deposited Ni film thickness of ~25 nm on Si(100) substrates. From the SEM analysis, morphological degradation of silicide starts at 700°C with the presence of holes as shown in Fig. 1b. When the as-deposited film thickness reduces to 15 nm, the onset of agglomeration starts at 600°C as shown in Fig. 1c and full agglomeration occurs at 700°C (Fig. 1d) on Si(100) substrates. Comparing Fig. 1b with Fig. 1c, a 100°C delay in the onset temperature of the morphological changes for a thicker NiSi is observed.

It has been suggested that the growth of voids in thin films occurs easily due to their high surface to volume ratio, and agglomeration can occur well below their melting points.⁶ Thermal grooves develop where grain boundaries intersect the surface of a film. Depending on the thickness of the films and grain size, a finite groove depth is possible. If the groove reaches the substrate, an equilibrium contact angle is established with respect to the substrate. For a given thickness of the film and density of the holes,⁷ at some critical contact angle (θ), a stable void forms in the film. The growth of the hole is driven by the reduction of the curvature created in the film edge profile. The films become discontinuous when a void impinges and islands of materials are formed. These islands then evolved into equilibrium shapes such as caps or beads. It can be seen that the thinner the silicide, the agglomeration phenomenon worsens.

Figures 2a-d show the SEMs of 25 and 15 nm thick Ni_{0.95}(Pt)_{0.05}

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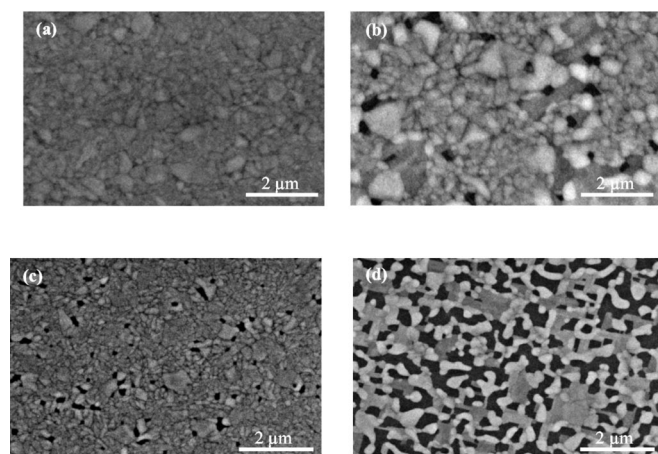


Figure 1. Top-view SEMs of NiSi formed on Si(100) substrates with 25 nm Ni film annealed at (a) 600 and (b) 700°C and 15 nm Ni film annealed at (c) 600 and (d) 700°C. The annealing duration was fixed at 30 s.

on Si(100) substrates after annealing at 600 and 700°C, respectively. Comparing the morphological changes to that of pure Ni silicide with similar thickness shown in Fig. 1, it can be seen that the addition of Pt has alleviated the tendency of agglomeration to a certain extent. Comparing Fig. 1b with Fig. 2b, and Fig. 1c with Fig. 2c, a 10% and 18% reduction in the hole distribution has been observed for the 25 and 15 nm as-deposited film after annealing at 600 and 700°C, respectively. The hole's evolution that precedes agglomeration is retarded. The effect of alloying element in the silicide morphology is seldom addressed, despite the fact that the grain boundary energy of a pure metal changes on alloying (therefore, silicide which behaves similarly to metal should assume this property). Generally, the grain boundary energy is reduced upon alloying; under these circumstances, the concentration of the alloying element is higher at grain boundaries than that in the matrix.⁸

Layer inversion.—Figures 3a and b show the RBS spectra of Ni and Ni_{0.95}(Pt)_{0.05} silicides formed with 25 nm of metal thin films on undoped poly-Si after annealing at 600°C. In another experiment, at 500°C, the Ni and Si signals in the RBS spectrum correspond to a composition ratio of NiSi with a thickness of ~36 nm (not shown, simulated with RUMP). At 600°C (Fig. 3a), the relatively high Si concentration at the surface indicates a degraded silicide coverage with exposed poly-Si grains. A tail at the Ni peak was observed at

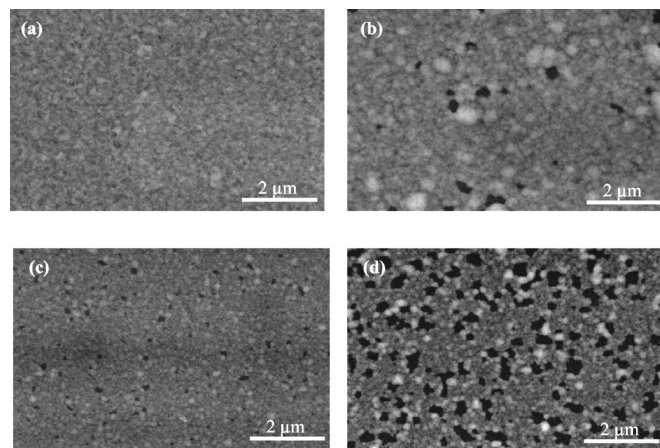


Figure 2. Top-view SEMs of Ni(Pt)Si formed on Si(100) substrates with 25 nm Ni(Pt) film annealed at (a) 600 and (b) 700°C and 15 nm Ni(Pt) film annealed at (c) 600 and (d) 700°C. The annealing duration was fixed at 30 s.

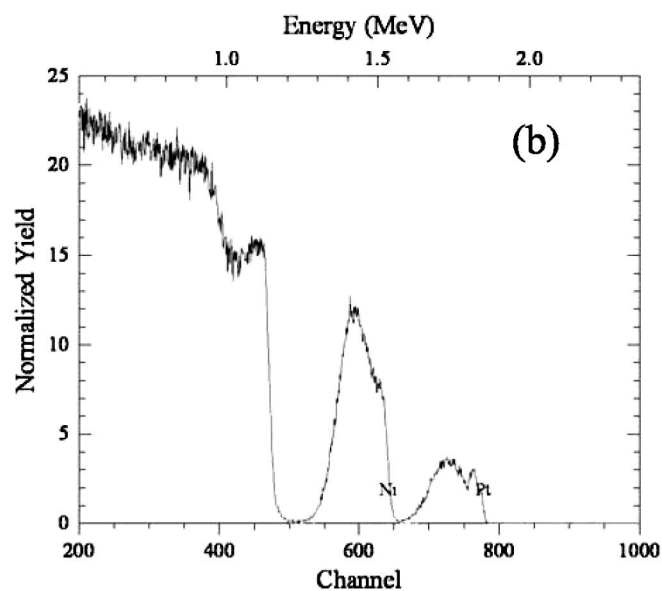
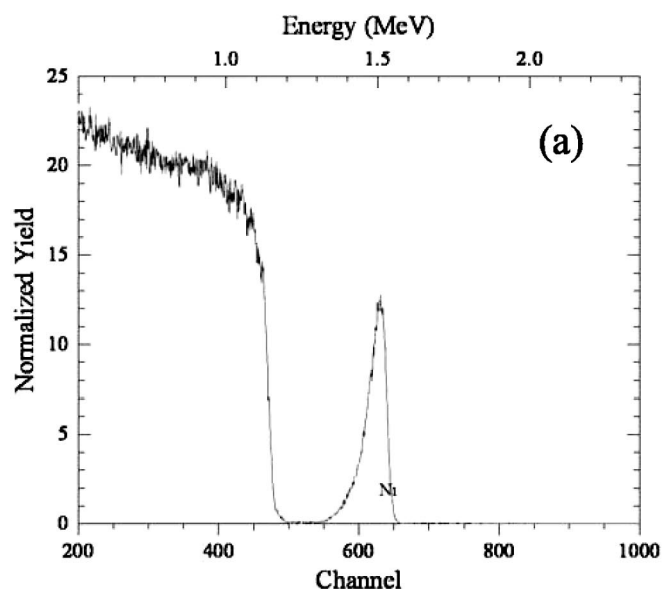


Figure 3. RBS spectra of (a) 25 nm as-deposited pure Ni on poly-Si, (b) 25 nm as-deposited Ni(Pt) on poly-Si, both after annealing at 600°C.

the low energy edge due to the rough silicide/Si interface. Figure 3b shows an increase in the Si to Ni and Pt ratio at 600°C, indicating a morphological degradation in the silicide layer. The Ni and Pt peak distribution shows a tendency of the accumulation of Ni and Pt at the poly-Si/gate oxide interface, which corresponds to the layer inversion behavior. These results are confirmed by the XTEM micrographs shown in Fig. 4a and b, in which the poly-Si inversion phenomenon is clearly seen with the silicide layer being “pushed-down” to the interface by the enhanced grain growth of the poly-Si after annealing at 600°C. The silicide remains to be monosilicide phase in both cases as indicated by electron diffraction and Raman analysis (not shown).

When the thickness of (Ni_{0.95}Pt_{0.05})Si being reduced to 20 nm by lowering the as-deposited Ni_{0.95}(Pt)_{0.05} thickness to ~10 nm, little or no layer inversion was observed on the poly-Si samples after

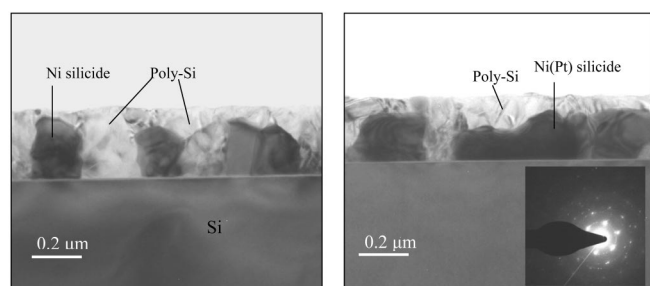


Figure 4. XTEM of (a) Ni and (b) Ni(Pt) on poly-Si after annealing at 600°C.

annealing at 600°C as shown in Fig. 5a. Compared with the previous results of ~58 nm Ni(Pt)Si formed at 600°C (Fig. 3b) at which layer inversion has occurred, this suggests that the layer inversion is affected by the thickness of the as-deposited metal; thicker film leads to a larger extent of inversion. At 700°C (Fig. 5b), the extent of layer inversion is similar to those in the thicker silicide at 600°C as shown in Fig. 3b.

As-deposited films of alloy Ni_{0.90}Pt_{0.10} sputtered onto poly-Si substrate is included to study the effect of Pt on layer inversion. Figures 6a and b show the SEM of 20 nm of (Ni_{0.95}Pt_{0.05})Si and (Ni_{0.90}Pt_{0.10})Si on poly-Si after annealing at 600°C. A surface coverage of the silicide is evidently improved with (Ni_{0.90}Pt_{0.10})Si formation compared to (Ni_{0.95}Pt_{0.05})Si, which demonstrates improved layer inversion when the Pt concentration is increased in the Ni(Pt) alloy silicides.

Discussion

Applying the model of agglomeration that considers the energy balance between the grain boundary energy (γ_{gb}), surface (γ_{fv}) and substrate interface energy (γ_i), it was shown that agglomeration should not occur if the grain size is below a critical value (L_c).⁹ This value increases with increasing film thickness, increasing surface and interface energy, and decreasing grain boundary energy. According to this model, a reduction of grain boundary energy associated with the presence of Pt in the grain boundaries will lead to a larger L_c that corresponds to the onset of agglomeration. However, the texture observed for Ni(Pt)Si on Si(100)¹⁰ should be an indication of a lower interfacial energy and thus should decrease the critical grain size. On the contrary, the texture relationship contributes to a lower grain boundary energy compared to the polycrystalline NiSi, resulting in a larger L_c .

As shown from the experimental results, agglomeration is preceded by the introduction of hole formation. The energy change associated with the introduction of holes includes both the interfacial energy ΔE^i and elastic energy ΔE^{el} and is given by $\Delta E = \Delta E^i + \Delta E^{el}$. For creating a circular cylindrical hole with radius R in a film of thickness h , ΔE^i is given by¹¹

$$\Delta E^i = \pi R^2(\gamma_{sv} - \gamma_{fs} - \gamma_{fv}) + 2\pi R h \gamma_{fv} = -2\pi R \gamma_i + 2\pi R h \gamma_{fv} \quad [1]$$

where γ_{sv} , γ_{fs} and γ_{fv} are the substrate/vapor interface energy, film/substrate interface energy and film/vapor interface energy, respectively.

The modification of the interfacial energy due to the texture relationship can also alter the agglomeration behavior in another way. The effect of interfacial energy on film morphology can be discussed by analogy with the classical problem of wetting of a substrate by a material in the stress free limit. For $\gamma_i = \gamma_{fs} + \gamma_{fv} - \gamma_{sv} \leq 0$, the island tends to spread, completely wetting the substrate. If $\gamma_i \geq 2\gamma_{fv}$, the island dewets the substrate or forms a sphere with minimum contact to the substrate. In an intermediate case, for $0 < \gamma_i$

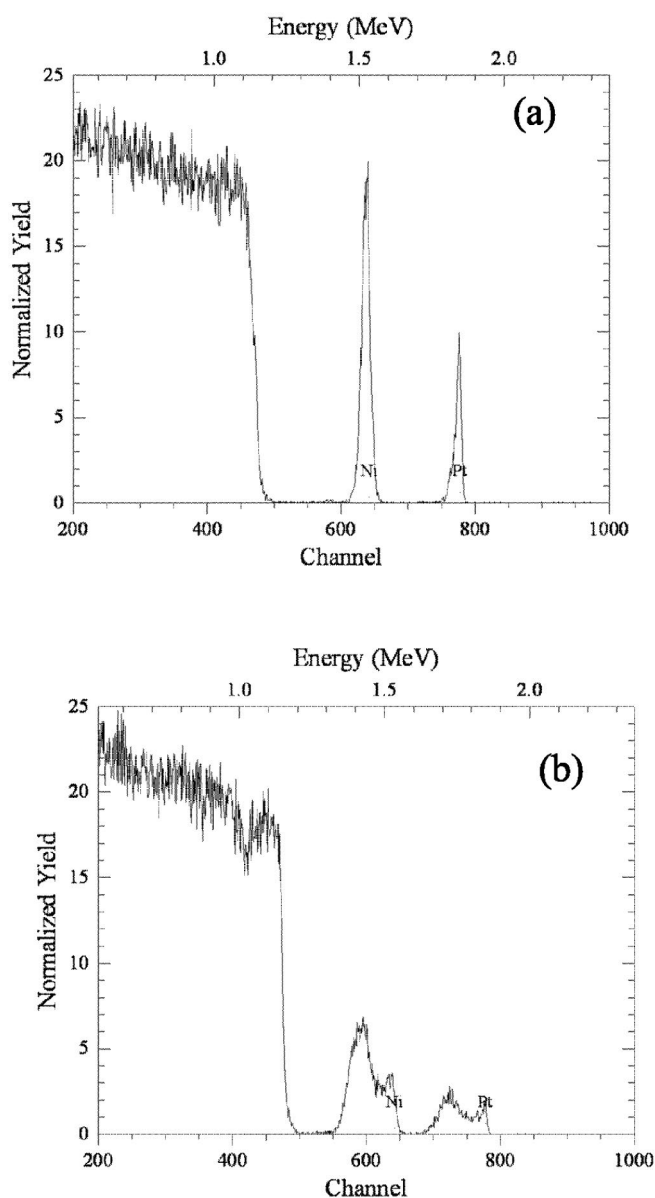


Figure 5. RBS spectra of a 20 nm Ni(Pt)Si on poly-Si after annealing at (a) 600 and (b) 700°C.

$< 2\gamma_{fv}$, the island meets the substrate at a wetting angle $0 < \theta < \pi$. The textured Ni(Pt)Si/Si(100) interface is expected to have a lower film/substrate interfacial energy, γ_{fs} , compared to the polycrystalline NiSi. A lower γ_{fs} favors wetting of the substrate (*i.e.*, reduced tendency of agglomeration). In addition, a lower driving

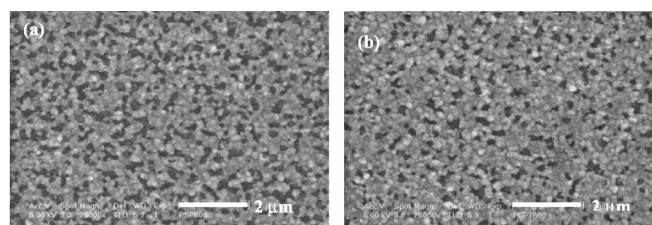


Figure 6. Top-view SEMs of silicide formation on poly-Si substrates with (a) Ni_{0.95}Pt_{0.05} (b) Ni_{0.90}Pt_{0.10} after annealing at 600°C.

force for hole evolution can also be derived according to Eq. 1.

It has been shown that for a given driving force the velocity of the random boundaries decreases rapidly with increasing alloy content, and only very low concentrations of alloy are required to change the grain boundary mobility by orders of magnitude.⁸ In fact, it has been found that the coherent twin boundary, in which the atoms fit perfectly into both grains, should be entirely immobile. Therefore, it can be expected that the mobility of the grain boundary will be lowered with more textured Ni(Pt)Si films. These factors hinder the hole evolution or agglomeration process. This was ascertained in the analysis of the slower normal grain growth in textured polycrystals, where some grains are of almost identical orientation, leading to grain boundaries with low angle, and hence both low energy and low mobility.¹²

Note that the addition of Pt has delayed the formation of NiSi₂ to a higher temperature (>750°C) despite the total reconstruction of the layer morphology. The enhanced phase stability is not disrupted by the total reconstruction of the morphology of the bilayer. After the layer inversion, the silicide grains residing on the gate oxide interface (as shown in Fig. 4) remain monosilicide. This indicates that the free energy change resulting from the addition of Pt is still very favorable to the monosilicide formation despite the high chance for NiSi₂ nucleation during the inversion of the layer topology.

The reduction of the surface energy and grain boundary energy is the driving force for poly-Si inversion. Poly-Si inversion may thus be affected by some other minor changes. The addition of impurities in the overlayer should modify the behavior by reducing some specific surface energy, or by reducing diffusion along the respective interfaces. However, the alloying of 5% Pt does not exert significant effect on the layer inversion, and thus does not seem to affect the driving force for poly-Si grain growth or the tendency to reduce the grain boundary energy. In a related work with the insertion of Pt layer in between Ni and poly-Si, the presence of Pt had no significant effect on the morphological stability.¹³ The fact that the degradation of Ni(Pt)Si on poly-Si occurs at similar temperatures as those of NiSi on poly-Si could be due to the Pt concentration is rather small (~5 atom %) and/or the extent of inversion or degradation mechanism is more dependent on the microstructure of the underlying substrate layer than the nature of the silicide top layer.¹⁴ The role of the substrates has previously been studied via the modifications of poly-Si microstructures by rapid thermal CVD growth and incorporation of ion implantation.^{15,16}

When the concentration of Pt is increased to 10 atom %, an improvement in the layer inversion is attained. Because the inversion process requires the deformation of silicides, the silicide plastic deformation temperature plays a role in the layer inversion; a higher deformation temperature of the silicide increases the onset temperature for grain growth in the poly-Si. Because PtSi has a relatively higher melting point compared to NiSi, the Ni(Pt)Si formed using a higher Pt concentration of as-deposited film exhibits relatively better resistance to layer inversion. In addition, it is shown in this work that thinner silicide is able to alleviate the extent of layer inversion. This is attributed to the final resultant stress by the top silicide layer

exerted on the underlying substrates. The thinner films with lesser stress exerted reduces the poly-Si grain boundary diffusion and therefore retards the layer inversion.

Conclusion

In summary, agglomeration was observed to be preceded by hole evolution during degradation of Ni or Ni(Pt) silicide morphology. It was found that the addition of 5 atom % of Pt has led to an improvement in the agglomeration behavior of NiSi and has little influence on the layer inversion on undoped poly-Si. Increasing the amount of Pt to 10 atom % is able to show improvement in the layer inversion behavior. The agglomeration behavior and layer inversion are discussed in terms of the controlling factors of grain boundary energy, interface energies and the nature of the silicides formed. Due to a reduced resultant stress of a thinner silicide, layer inversion on poly-Si is also found to be less severe for thinner silicide of ~20 nm.

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